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## Outgassing in the LiD/LiOH system

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### **ABSTRACT**

Temperature programmed decomposition (TPD), scanning electron microscopy (SEM) and x-ray diffraction (XRD) were performed on lithium hydroxide (LiOH) polycrystallites and LiD/LiOH composite nanocrystals. Our studies revealed that LiOH grains are thermally decomposed into Li<sub>2</sub>O, releasing water, following a three dimensional phase boundary movement from the surface inward. The rate of H<sub>2</sub>O released is controlled by a rate constant that is expressed as:

$$\frac{d\alpha}{dt} = \nu \cdot e^{-(E/RT)} \cdot f(\alpha)$$

where  $t$  is time;  $\alpha$  is the reacted fraction (0 to 1);  $\nu$  is the pre-exponential factor which includes many constants describing the initial state of the sample such as three dimensional shape factors of initial particles, molecular mass, density, stoichiometric factors of chemical reaction, active surface and number of lattice imperfections, and so forth;  $E$  is the activation energy for the rate controlling process,  $R$  is the gas molar constant, and  $f(\alpha)$  is an analytical function which is determined by the rate-limiting reaction mechanism (random nucleation, diffusion, phase boundary motion, etc.) [1-5].

Due to fewer neighboring bonds at the surface, surface lithium hydroxide decomposes at low activation energies of  $\sim 86$ - $92$  kJ/mol with corresponding pre-exponential factors of  $\sim 2.7 \times 10^6$ - $1.2 \times 10^7$  s<sup>-1</sup>. Near-surface hydroxide, having bonding much like bulk hydroxide but experiencing more stress/strain, decomposes at activation energies of  $\sim 89$ - $108$  kJ/mol with corresponding pre-exponential factors of  $\sim 9.5 \times 10^5$ - $9.3 \times 10^7$  s<sup>-1</sup>. Bulk lithium hydroxide, however, decomposes at higher activation energies of  $\sim 115$ - $142$  kJ/mol with corresponding pre-exponential factors of  $\sim 4.8 \times 10^6$ - $1.2 \times 10^9$  s<sup>-1</sup>. Bulk lithium hydroxide is very stable if stored at room temperature. However, lithium hydroxide molecules at or near the surface of the grains slowly decompose, in a vacuum or dry environment at room temperature, into Li<sub>2</sub>O releasing water over many decades. These surface and near-surface molecules account for a few percent of the total lithium hydroxide with micrometer grain size. Experimental data also confirm that the conversion of Li<sub>2</sub>O grains back to lithium hydroxide during moisture exposure proceeds from the surface inward such that surface states are always filled before bulk states.

In a different set of experiments, nanometer scale composite grains composed of LiD inner cores and LiOH outer layers were observed to form on top of pressed polycrystalline LiD upon moisture exposure. Experimental data suggest that the long-term outgassing effects of surface states in these composite hydroxide nanocrystals, which have very high ratios of surface molecules to bulk molecules, are much more significant than in the case of micrometer grain (bulk) hydroxide. The measured kinetics in this work enable the construction of the evolution steps in these composite nanocrystals in a dry environment as a function of time.

Our investigation also confirmed that vacuum heating of the LiD/LiOH composite nanocrystals converts most of LiOH into Li<sub>2</sub>O. Subsequent moisture re-exposure at up to 50 ppm for many days converts only surface and near surface Li<sub>2</sub>O to surface and near surface LiOH.

## **INTRODUCTION**

Based on the phase diagram for LiH/LiOH/Li<sub>2</sub>O, bulk lithium hydroxide is very stable even when kept in a dry environment [1-3]. However, our recent experiments suggest that, depending on the formation conditions, certain types of lithium hydroxide grown on LiD can slowly decompose in a dry environment over a period of years to decades [4]. We later associated these unstable hydroxide structures with surface and near surface LiOH [5]. In ref. [5], we also reported the formation of nanometer scale composite grains composed of LiD inner cores and LiOH outer layers on top of pressed polycrystalline LiD upon moisture exposure. The effects of LiOH surface states are strongly pronounced in the LiD/LiOH composite nano-system. The diffusion coefficient for the diffusion controlled reaction of lithium hydroxide with LiD at the hydroxide/Li<sub>2</sub>O/LiD interface in the composite nanocrystal powder in dry environments was also estimated.

In this report, these findings and our updated experimental results are employed to present the stability of the LiD/LiOH composite nanocrystals system in a dry environment and the effects of moisture re-exposure on the dry-heated LiD/LiOH nano-composite system.

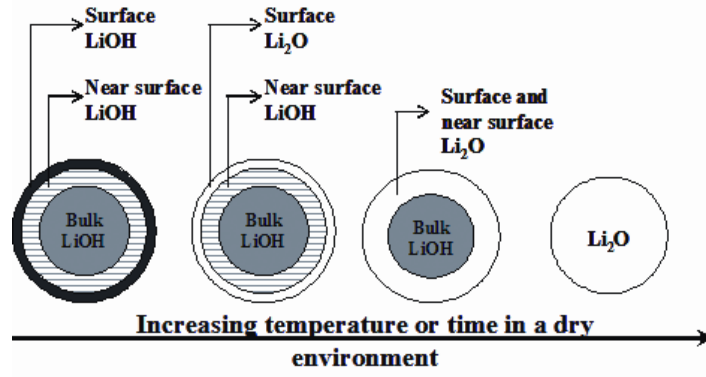
## **EXPERIMENTAL METHODS and ANALYSIS TECHNIQUES**

Our experimental investigation on the stability of the LiD/LiOH system involved temperature programmed decomposition (TPD), scanning electron microscopy (SEM) and x-ray diffraction (XRD). The details of the experimental methods and analysis techniques can be found in ref. [5].

## **RESULTS & DISCUSSION**

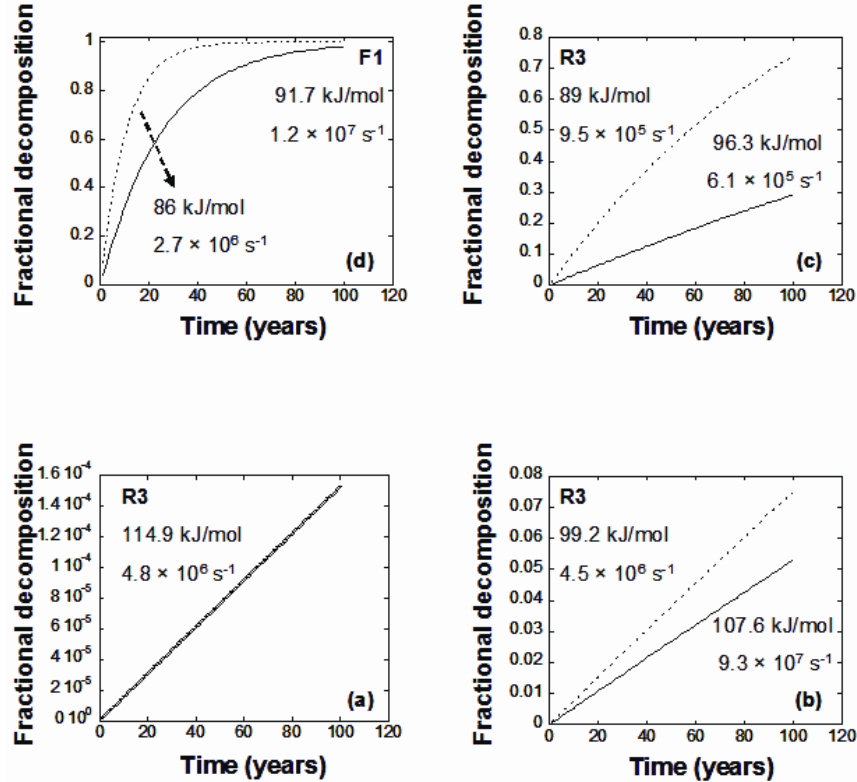
### **Thermal decomposition of lithium hydroxide polycrystals and nanocrystals:**

The decomposition of LiOH with micrometer grain sizes has been reported to be rate limited by a three dimensional phase boundary motion (R3) moving inward from the surface [3-4], with an activation energy on the order of 92 [3], or 122 -149 kJ/mol [4]. Myers reported an activation energy for the decomposition of LiOH grown on single crystal of 130 kJ/mol [1]. Unfortunately, references [1] and [3] did not report the associated pre-exponential factors which are required to sufficiently model the decomposition of LiOH at any given temperature as a function of time. In references [4] and [5], we supplied the pre-exponential factor together with activation energy and rate-limiting mechanism for the decomposition of LiOH microcrystals and nanocrystals. In short, LiOH decomposes from the surface inward. In this case, surface LiOH at the vacuum/LiOH interface is the first to be converted to surface Li<sub>2</sub>O, then near-surface LiOH and finally bulk LiOH are converted to Li<sub>2</sub>O. As a result of having fewer bonds to break at the vacuum/LiOH interface, surface LiOH is expected to decompose more easily than its bulk counterpart. In the near-surface region, the hydroxide lattice is distorted causing LiOH molecules in this region to decompose somewhat more easily than bulk material. The cartoon on the left of Fig. 1 illustrates the decomposition process of a LiOH (spherical) grain from the surface inward. This predicted increase in activation energy as the decomposition process proceeds inward is reflected in the isoconversion plot presented in the plot on the right of Fig. 1. The activation energies for the thermal decomposition of LiOH increase from ~ 86-92 kJ/mol with corresponding pre-exponential factors of  $\sim 2.7 \times 10^6$ - $1.2 \times 10^7$  s<sup>-1</sup> for surface LiOH, to ~89-108 kJ/mol with corresponding pre-exponential factors of  $\sim 9.5 \times 10^5$ - $9.3 \times 10^7$  s<sup>-1</sup> for near-surface LiOH, and to ~ 115-142 kJ/mol with corresponding pre-exponential factors of  $\sim 4.8 \times 10^6$ - $1.2 \times 10^9$  s<sup>-1</sup> for bulk LiOH.



**Fig. 1.** The decomposition process of a LiOH (spherical) grain from the surface inward.

Fig. 2 shows the simulated decomposition spectra, at 300 K as a function of time, of (a) bulk LiOH with  $E = 114.9$  kJ/mol and  $\nu = 4.8 \times 10^6$  s<sup>-1</sup> according to the R3 model; (b) near-surface LiOH with  $E = 99.2$  kJ/mol and  $\nu = 4.5 \times 10^6$  s<sup>-1</sup> (dashed line) and with  $E = 107.6$  kJ/mol and  $\nu = 4.5 \times 10^6$  s<sup>-1</sup> (solid line) according to the R3 model; (c) even nearer surface LiOH with  $E = 89$  kJ/mol and  $\nu = 9.5 \times 10^5$  s<sup>-1</sup> (dashed line) and with  $E = 96.3$  kJ/mol and  $\nu = 6.1 \times 10^5$  s<sup>-1</sup> (solid line) according to the R3 model; and (d) surface LiOH with  $E = 86$  kJ/mol and  $\nu = 2.7 \times 10^6$  s<sup>-1</sup> (dashed line) and with  $E = 91.7$  kJ/mol and  $\nu = 1.2 \times 10^7$  s<sup>-1</sup> (solid line) according to the F1 model (or surface decomposition model as presented in Ref. [5]). In fig. 2(b), (c) and (d), the dashed and solid lines represent the upper and lower limits of decomposition for the corresponding types of LiOH.

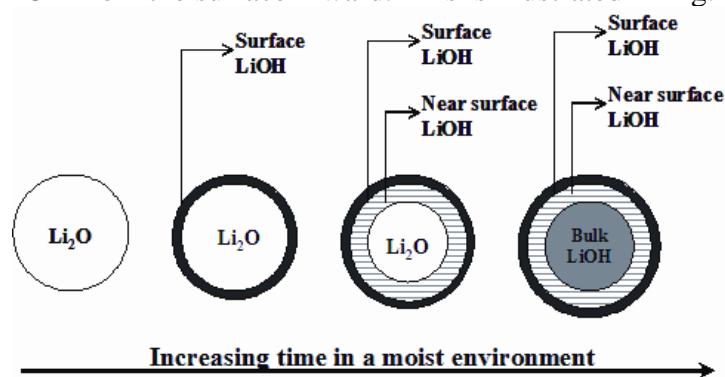


**Fig. 2.** Simulated decomposition spectra, at 300 K as a function of time, of (a) bulk LiOH according to R3 model; (b) of near-surface LiOH according to the R3 model; (c) of even nearer-surface LiOH according to the R3 model; and (d) of surface LiOH according to the F1 model.

Clearly, in contrast with bulk LiOH, surface and near-surface LiOH are not stable and would start to decompose in a dry environment into  $\text{Li}_2\text{O}$ , releasing  $\text{H}_2\text{O}$  over a period of many decades. It is important to note that the ratio of surface and near-surface states to bulk states in LiOH structures with grains on the order of tens of micrometers is rather small ( $\sim 0.03$ ). However, exposure of pressed polycrystalline LiD to moisture forms composite nanocrystals with LiD inner cores and LiOH outer layers [5]. The effects of decomposition of low activation energy surface and near-surface states in these hydroxide nanocrystals are much more pronounced than in the case for LiOH microcrystals. In a closed and dry system containing both LiD and LiOH, water released from the decomposition of surface and near-surface LiOH ultimately reacts with LiD to form hydrogenous species.

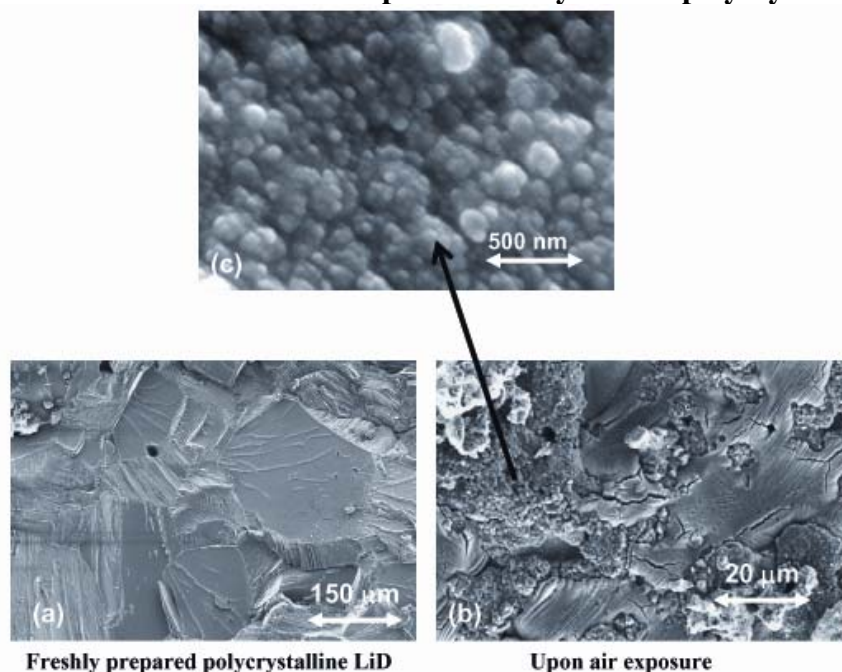
#### **The effects of moisture re-exposure on the dry-heated LiOH:**

In ref. [5], it has been established that upon moisture exposure,  $\text{Li}_2\text{O}$  grains are converted back to LiOH from the surface inward. This is illustrated in Fig. 3.



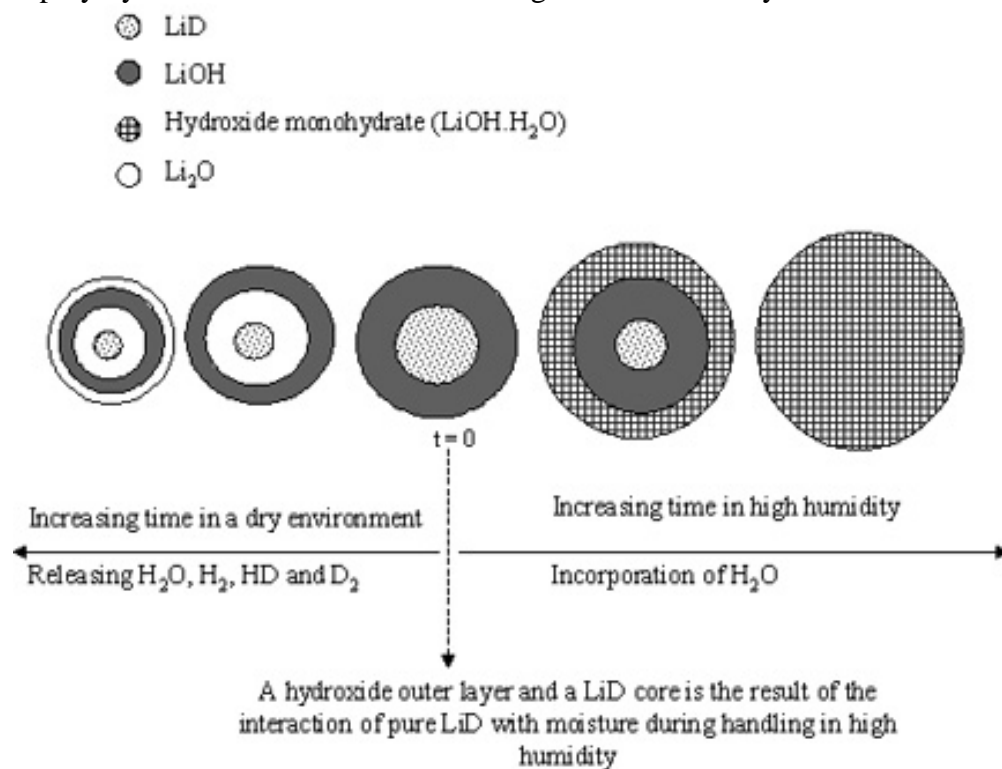
**Fig. 3.** An illustration of the inward re-hydroxylation process for  $\text{Li}_2\text{O}$ .

#### **The effects of low levels of moisture re-exposure on dry-heated polycrystalline LiD:**



**Fig. 4.** (a) SEM image of a freshly cut polycrystalline LiD sample with grain sizes on the order of hundreds of micrometers; (b) A layer of nanostructures with grain sizes on the order of tens of nanometers was seen to form on top of the polycrystalline LiD sample after air exposure; (c) An area of (b) at a higher resolution.

It was observed with SEM that exposing pressed polycrystalline LiD to moisture resulted in the formation of nanometer scale grains. Fig. 4(a) shows the SEM image of a freshly cut polycrystalline LiD sample with grain sizes on the order of hundreds of micrometers. Upon exposure to air during handling, a layer of nanocrystalline hydroxide with grain sizes on the order of tens of nanometers was seen to form on top of the polycrystalline LiD sample [fig. 4(b) and (c)]. Scraping the surface of the pressed polycrystalline LiD with a razor blade produced powder composed of LiD nanocrystalline cores and outer layers of LiOH as evidenced by XRD [5]. XRD and SEM confirmed that the scraped off powder was composed of nanocrystalline LiD inner cores with an average size of 35 nm covered with lithium hydroxide outer layers. After about 2 hours of air exposure, some lithium hydroxide began to transform into  $\text{LiOH}\cdot\text{H}_2\text{O}$ . Since the surface to volume ratio in nanometer scale grains is drastically increased in comparison with that in micrometer scale grains, the ratio of unstable surface and near-surface hydroxide to stable bulk hydroxide is significantly higher in the composite hydroxide/LiD nanocrystals formed on polycrystalline LiD than in the micrometer scale hydroxide grains [5]. Fig.5 illustrates the evolution of a composite nanocrystalline grain formed on pressed polycrystalline LiD as a result of storage in moist and dry environments.

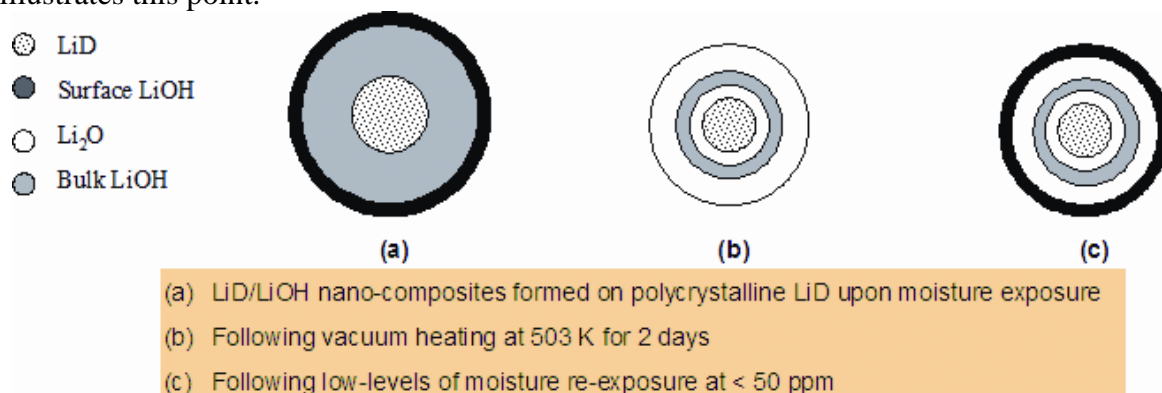


**Fig. 5.** An illustration of the evolution of a nanocrystalline grain formed on pressed polycrystalline LiD as a result of storage in moist and dry environments.

The moisture exposure originally breaks the surface of these pressed polycrystalline LiD grains into nanocrystals composed of LiD cores and outer layers of LiOH. With increasing exposure time and/or humidity level,  $\text{LiOH}\cdot\text{H}_2\text{O}$  begins to form until eventually all these nanocrystals are  $\text{LiOH}\cdot\text{H}_2\text{O}$ . However, if the nanocrystals formed on pressed polycrystalline LiD were to be stored in a vacuum or dry environment, a buffer layer of  $\text{Li}_2\text{O}$  was experimentally found to form in each nanocrystal between the LiD core and the hydroxide outer layer [5,6]. This is a result of the reaction of LiD with LiOH to form  $\text{Li}_2\text{O}$ , releasing  $\text{H}_2$ , HD and

D<sub>2</sub>. Even after the formation of a Li<sub>2</sub>O buffer layer, the solid state diffusion of LiOH through this buffer layer to react with LiD (or vice versa) continues to thicken the Li<sub>2</sub>O buffer zone. With increasing time in dry environments, surface and near-surface LiOH species, which are unstable, would in turn decompose to form Li<sub>2</sub>O near the LiOH/vacuum interface and the LiOH/Li<sub>2</sub>O interface (left most image in Fig. 5).

Recently, we have performed experiments in which LiD/LiOH nano-composites (scrapped off the surface of polycrystalline LiD in air) were heated in vacuum to 503 K for 2 days. Our TPD results indicated that most of the LiOH (> 90%) in the nano-composites has been converted to Li<sub>2</sub>O. Upon subsequent re-exposure up to 50 ppm of H<sub>2</sub>O for many days, only surface and near-surface Li<sub>2</sub>O has been converted back to surface and near-surface LiOH. Fig. 6 illustrates this point.



**Fig. 6.** Re-hydroxylation at low levels of moisture exposure following vacuum heating of the LiD/LiOH nano-composite at 503 K.

## **CONCLUSIONS**

The decomposition of LiOH powder is consistent with a 3D phase boundary motion from the surface inward. The activation energies for the thermal decomposition increase from ~ 86-92 kJ/mol with corresponding pre-exponential factors of  $\sim 2.7 \times 10^6$ - $1.2 \times 10^7$  s<sup>-1</sup> for surface LiOH, to ~89-108 kJ/mol with corresponding pre-exponential factors of  $\sim 9.5 \times 10^5$ - $9.3 \times 10^7$  s<sup>-1</sup> for near-surface LiOH, and to ~ 115-142 kJ/mol with corresponding pre-exponential factors of  $\sim 4.8 \times 10^6$ - $1.2 \times 10^9$  s<sup>-1</sup> for bulk LiOH. Bulk LiOH is thermally stable even when stored in dry conditions at room temperature for more than 100 years, while surface and near-surface LiOH significantly decompose in a similar environment in a matter of decades. The ratio of surface and near-surface states to bulk states in micrometer scale LiOH grains was experimentally measured to be only a few percent. However, exposure of pressed polycrystalline LiD to moisture forms composite nanocrystals with LiD inner cores and LiOH outer layers. The effects of decomposition of low activation energy surface and near-surface states in these hydroxide nanocrystals are much more pronounced than in the case for LiOH microcrystals. In a closed and dry system containing both LiD and LiOH, water released from the decomposition of surface and near-surface LiOH ultimately reacts with LiD to form hydrogenous species. Our investigation also confirmed that vacuum heating of the LiD/LiOH composite nanocrystals converts most of LiOH into Li<sub>2</sub>O. Subsequent moisture re-exposure at up to 50 ppm for many days converts only surface and near surface Li<sub>2</sub>O to surface and near surface LiOH.

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